

Thermophysical Databank for Technically Important Gases and Liquids¹

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ABSTRACT

Thermophysical databank for technically important gases and liquids was created. It provides users with data for near thirty substances: monatomic and diatomic gases, air, water and steam, carbon dioxide, ammonia, some hydrocarbons and refrigerants. The coefficients of equations of state and equations for calculating transport properties, the ideal-gas functions, the saturated vapor pressure and the melting pressure are kept for each substance.

The system of programs ensures the calculation of compressibility factor, density, enthalpy, entropy, isochoric and isobaric specific heat, speed of sound, Joule-Thomson coefficient, viscosity, thermal conductivity and some other properties. These values can be determined in the single-phase and two-phase regions and on the phase-equilibrium lines at temperatures from the triple point up to 500 – 1500 K and at pressures up to 100 MPa (for monatomic and diatomic gases – up to 2500 – 3000 K and 300 MPa). Properties can be calculated at following nine combinations of independent variables: T, ρ ; T, p ; T, s ; T, x ; p, ρ ; p, h ; p, s ; p, x ; h, s . The software of the bank has a module structure and permits to enlarge the nomenclature of substances, properties and independent variables.

KEY WORDS: databank; gases; liquids; high pressures; thermophysical properties.

1. INTRODUCTION

Reliable data on thermophysical properties of substances are necessary for many scientists, engineers and students. For solving many practical tasks these data should be presented at different independent variables and at various values of these variables. Therefore the creation of a new type of informative systems – the databanks – acquired special importance. In contrast to the usual informative searching systems the databanks allow not only to take up the keeping data but also to get new results on the basis of equations, used in these banks, with the help of logical and mathematical operations.

2. THE DATABANK

2.1 General description

We created thermophysical databank for technically important gases and liquids. It provides users with data for near thirty substances: monatomic and diatomic gases, air, water and steam, carbon dioxide, ammonia, some hydrocarbons and refrigerants. The informative massifs are the set of program modules and the blocks of numeric data. For calculating thermodynamic properties of a substance most often the unified equation of state for gas and liquid is used. For a series of substances side by side with unified equations of state the virial equations for gaseous phase which are valid at high temperatures (300 – 3000 K) are used also. In some cases for greater reliability two forms of equation of state can be applied, and users have the possibility to chose any of them. The dependences of viscosity and thermal conductivity on temperature and density are used for calculation of transport properties.

The coefficients of equations of state and equations for the transport properties are kept for each substance. Parameters of the critical point and coefficients of equations for calculation of the ideal-gas functions, the saturated vapor pressure and the melting

pressure are kept also. For the majority of substances reliable equations of state were employed that describe the experimental data with high accuracy. Most of these equations were used by their authors for calculating the tables of reference data.

The system of programs consists of the following main functional blocks:

block of input of initial data (choosing the substance, the independent parameters, the units of measurements); block of choosing the mode of calculation (single calculation or step-wise calculations with a given number of steps); block of calculating the properties of substances; block of output of the results; block of saving, editing and printing the results; block of presenting the information in a graphic form.

The mentioned programs ensure the calculation of compressibility factor, specific volume, density, enthalpy, internal energy, entropy, isochoric and isobaric specific heat, speed of sound, Joule-Thomson coefficient, adiabatic exponent, volume expansion coefficient, thermal pressure coefficient, saturated vapor pressure, heat of vaporization, dynamic and kinematic viscosity, thermal conductivity, temperature conductivity and Prandtl number. The values of properties can be determined in the single-phase region, on the phase-equilibrium lines and in the two-phase region at temperatures from the triple point up to 500 – 1500 K and at pressures up to 100 MPa (for monatomic and diatomic gases – up to 2500 – 3000 K and 300 MPa, for some substances - up to higher pressures).

2.2. The used equations

The difficulty at constructing the databank appeared due to existence of different forms of empirical equations describing the experimental data on thermophysical properties of substances. We used in most cases the equation of state having so-called polynomial form, which is convenient for fast calculation of various properties

$$Z = 1 + \sum_{i=1}^m \sum_{j=0}^{s_i} b_{i,j} \frac{\omega^i}{\tau^j}, \quad (1)$$

where $Z = pv / RT$ is the compressibility factor, $\omega = \rho / \rho_{cr}$ is the reduced density, and $\tau = T / T_{cr}$ is the reduced temperature.

The equations of state for gases valid in the high-temperature region have the same form (1), but in these equations theoretical grounded virial coefficients are used. This circumstance ensures the extrapolation by means of these equations in the region where the experimental data are absent.

For some well-investigated substances so-called fundamental equation of state is used also. This equation has the form

$$\Phi = \frac{A}{RT} = \alpha_0(\omega, \tau) + \alpha(\omega, \tau), \quad (2)$$

where A/RT is the dimensionless Helmholtz energy, $\alpha_0(\omega, \tau)$ is the ideal-gas part of Φ and $\alpha(\omega, \tau)$ is the real part of Φ .

The function $\alpha(\omega, \tau)$ may be represented in the form

$$\alpha(\omega, \tau) = \sum_{i=1}^m \sum_{j=0}^{s_i} b_{i,j} \frac{\omega^i}{\tau^j} + \exp(-\gamma\omega^2) \sum_{i=1}^n \sum_{j=1}^{r_i} c_{i,j} \frac{\omega^i}{\tau^j}, \quad (3)$$

or in more complicated form containing different powers of ω in the exponential terms.

The advantage of equation (2) is the possibility to calculate all thermodynamic properties only by differentiation of the function $\Phi(\omega, \tau)$.

The equations describing the data of viscosity and thermal conductivity and data on ideal-gas functions and on saturated vapor pressure and melting pressure have different forms for various substances. This circumstance was taken into account at elaboration the programs for the databank. Finally the bank was constructed with use of

equations of state in forms (1) or (2) in vast majority cases and various forms of equations, describing the transport properties, ideal-gas functions and data on saturation line. The literature sources from which the used equations were taken are given in Table 1. In this table the intervals of temperatures and maximum values of density and pressure for each equation are indicated also.

2.3. Calculation of properties

At elaboration of algorithms and programs for the calculation of thermophysical properties we took into account the specific demands which are connected with designing power and refrigerating plants. While the designing the properties are calculated repeatedly at different systems of independent variables. Therefore the main demand for the thermophysical databank is the reliability and internal agreement of calculated values of properties in all points of thermodynamic surface by different combinations of independent parameters. This demand was ensured by use of reliable equations of state and equations for calculating transport properties for each substance.

A great significance has the speed of calculations and minimum volume of used memory. The quick calculation of thermophysical properties is performed by elaboration of optimum algorithms as a whole and of separate procedures most often used at calculations (e.g. the determination of reduced density for given values of temperature and pressure). For economy of memory the module principle of programming was taken with unified use of modules.

At calculating the working processes of chemical, power and refrigerating plants the values of thermophysical properties at different independent variables are necessary. Therefore at creation of the databank a great attention was paid to the compiling of programs for calculating the thermophysical properties by various

combinations of independent variables, not only as function of temperature and pressure. Properties can be calculated at following nine combinations of independent variables: T, ρ ; T, p ; T, s ; T, x ; p, ρ ; p, h ; p, s ; p, x and h, s .

The problem of calculating thermophysical properties at different independent variables arises due to the reason, that in equation of state the density and temperature have a degree more than three. Therefore it is necessary to use the iterative methods of determining the values of these parameters.

At calculating the properties in coordinates T, p and T, s it is necessary to determine preliminary the second independent parameter used in the equation of state (and in equations for transport properties) – the density. To determine the density in coordinates T, p Newton's method is used, that is very efficient in all the field of state parameters except the vicinity of the critical point. The necessary initial values of density are determined from the unified relations depending on the field where the given point is located (gas or liquid). If Newton method does not converge, the method of bisection is joined automatically. The density in coordinates T, s is determined on the given isotherm by way of the iteration. That ensures the accordance of the given value s with the value calculated from the equation of state.

For calculating the properties in coordinates T, x or p, x first of all the properties on the saturation line are calculated. The necessary values of pressure (or temperature) and densities of saturated vapor and liquid are calculated by means of unified equation of state on the basis of Maxwell's rule.

At calculating the properties in coordinates p, ρ it is necessary to determine preliminary the temperature and in coordinates p, h and p, s – both the independent variables of the equation of state: temperature and density. Therefore in the first case a single iterative cycle is employed and in the second case – the double iterative cycle.

The temperature in coordinates p, ρ is determined by iteration on the given isochore by the method of bisection and in coordinates p, h and p, s by the method of direct iteration on the isobar on the basis of known thermodynamic relations. The values of density necessary for calculation of caloric properties (h or s) are determined for a given pressure and the iterative temperature by means of above-mentioned procedure of determining the density in coordinates T, p . The iterative calculations for determining T and ρ are going on until admissible errors of density, enthalpy and entropy are reached.

The coordinates h, s are the most complicated for defining the position of the calculated point on thermodynamic surface. It happens because neither of three thermal parameters connected with the equation of state is given in this case. Therefore the algorithm of calculation of thermophysical properties in coordinates h, s is based on a relative comparison of given and calculated values of enthalpy on the given isentrope. According to this algorithm the point of intersection of the isentrope with the saturation line is defined first. Then the iterative calculations are fulfilled in single-phase or two-phase region depending on given value of enthalpy.

The system of programs formed on the basis of the mentioned algorithms showed its efficiency. Calculations carried out for many substances that are used as working media of power and refrigerating plants showed not only the coincidence of the calculated properties at different combinations of independent variables, but also their high internal agreement in all the single-phase region, metastable states and in the two-phase region. To ensure such agreement of properties the following values of admissible errors were applied: density 0,001%, enthalpy 0,05 kJ/kmol and entropy 0,005 kJ/(kmol.K). The time of calculations of one and the same set of properties depends upon the system of parameters and increases at 2–4 times in coordinates p, h and p, s and at 10–20 times in coordinates h, s in comparison with coordinates T, p . It

should be noted, that calculations of properties can be fulfilled also on the given isoline at a chosen step of the second independent parameter and a chosen number of steps.

The software of the bank, having a module structure, permits to enlarge the nomenclature of substances, calculated properties and independent variables. Now we work on inclusion in our bank the published experimental data on thermodynamic and transport properties of above-mentioned substances and equations for calculation of thermophysical properties for new substances.

3. CONCLUSIONS

The elaborated databank is effectively used at calculating the processes of chemical, power and refrigerating plants. Its possibilities are larger than possibilities of usually used printed reference-books. First, the high speed of receiving the information on properties of substances in different coordinates should be noted. The part of mentioned system of programs can be used separately for constructing the programs for concrete aims, e.g. for calculation of heat-exchanging apparatus of air-separating installations. Therefore, with the help of created databank the working place of a designer or a technologist can be rearranged.

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Table 1. List of substances, included in the databank, sources of equations
and intervals of parameters for calculating thermophysical properties

Substances	Sources of equations		Temperature range ΔT , K	Maximum density, kg/m^3	Maximum pressure, MPa
	for therm. properties	for transp. properties			
Argon	[1]		84 – 1300	1500	100
	[2]		84 – 1200	1830	1000
		[3]	84 – 1300	1500	100
	[4]	[4]	373 – 3000	400	300
Helium	[5]		2 – 1500	300	100
		[6]	2 – 1000	300	100
Krypton	[7]		120 – 1300	2570	100
		[3]	120 – 1300	2570	100
	[4]	[4]	273 – 3000	600	220
Neon	[3]	[3]	25 – 1300	1400	100
	[4]	[4]	200 – 3000	300	400
Xenon	[3]	[3]	161 – 1300	3100	100
	[4]	[4]	323 – 3000	600	120
Carbon oxide	[4]	[4]	323 – 2250	600	220
Fluorine	[4]	[4]	300 – 1000	550	160
Hydrogen	[4]	[4]	273 – 2500	300	350
Nitrogen	[8]		65 – 1500	920	100
		[9]	65 – 1000	920	200
	[4]	[4]	273 – 2500	330	300

Table 1. (continuation)

Substances	Sources of equations		Temperature range ΔT , K	Maximum density, kg/m^3	Maximum pressure, MPa
	for therm. properties	for transp. properties			
Nitrogen oxide	[4]	[4]	273 – 2000	400	280
Oxygen	[10]		55 – 1500	1350	100
		[11]	70 – 500	1340	100
	[4]	[4]	500 – 2500	300	280
Air	[12]		70 – 1500	1020	100
		[13]	150 – 1000	850	100
	[4]		323 – 2500	320	300
Ammonia	[14]		195 – 750	750	50
		[15]	195 – 600	850	1000
Carbon dioxide	[16]	[16]	220 – 1300	1300	200
	[17]		216 – 1100	1450	800
	[4]	[4]	573 – 2500	300	180
Water and	[18]		273 – 1073	1220	1000
steam	[19]		252 – 1273	2150	25000
n-Butane	[20]		135 – 700	750	100
Ethane	[21]		91 – 700	660	80
Ethylene	[22]		110 – 600	700	300
Methane	[23]		91 – 1000	480	100
	[24]		91 – 625	580	1000
		[25]	91 – 1000	480	100
Propane	[26]		100 – 700	720	100

Table 1. (continuation)

Substances	Sources of equations		Temperature range ΔT , K	Maximum density, kg/m^3	Maximum pressure, MPa
	for therm. properties	for transp. properties			
R11	[27]		223 – 470	180	3
R12	[27]		173 – 453	960	18
R13	[27]		173 – 383	1070	10
R21	[28]	[28]	303 – 473	1400	20
R22	[28]	[28]	233 – 473	1340	20
R23	[28]	[28]	233 – 473	1340	20
R32	[29]		140 – 500	1420	70
R125	[29]		180 – 500	1680	70
R142	[27]		243 – 433	250	4
R502	[27]		173 – 423	1020	15